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PHASE COMPOSITION OF POWDERED MATERIAL BASED ON CALCIUM HYDROXYAPATITE AND SODIUM DIHYDROPHOSPHATE

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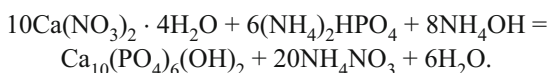
Powder mixtures based on calcium hydroxyapatite (HAP) and sodium dihydrophosphate are investigated. It is established that calcium phosphates with Ca : P = 1 are formed in these mixtures as a result of mechanochemical activation. On heating each component of the mixture undergoes a change: HAP (Ca : P = 1.67) partially transforms into tricalcium phosphate (Ca : P = 1.5), the low-temperature calcium phosphates brushite and monetite (Ca : P = 1) transform into calcium pyrophosphate, NaH_2PO_4 transforms into NaPO_3 , and Na_2HPO_4 transforms into $\text{Na}_4\text{P}_2\text{O}_7$. In the process the components interact with one another with double sodium calcium ortho- and metaphosphates being formed.

Key words: calcium hydroxyapatite, sodium dihydrophosphate, powders, heat treatment, phase composition.

Composite ceramic materials containing as a resistive hydroxyapatite (HAP) phase, which is stable against dissolution, and a resorbable phase are needed to heal bone-tissue defects. As a rule, tricalcium phosphate (TCP) $\text{Ca}_3(\text{PO}_4)_2$ is used as the resorbable phase. A series of publications is devoted to the development of materials containing as the resorbable phase calcium pyrophosphate (CPP) $\text{Ca}_2\text{P}_2\text{O}_7$ and renanite NaCaP_4 (US Patent No. 7037867) [1–4]. It is well known that pyrophosphate ions as well as polyphosphate ions participate in the regulation of many biological processes [5]. However, there is only limited information on obtaining ceramic composite materials containing polyphosphates. Sodium polyphosphates are formed, for example, when sodium dihydrophosphate NaH_2PO_4 is heated [6].

Our objective in the present work was to investigate the interaction of the components of a powder system: HAP and NaH_2PO_4 . The composition and properties of the mixtures investigated are presented in Table 1.

HAP powder was synthesized according to the reaction



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A 0.3 M water solution of ammonium hydrophosphate $(\text{NH}_4)_2\text{HPO}_4$ was added in drops to 1 liter of a 0.5 M solution of calcium nitrate $\text{Ca}(\text{NO}_3)_2$ over 40 min. The reaction was conducted at temperature 60°C with intense mixing; the pH was maintained at 8, adding 25% water solution of NH_3 . The HAP obtained was separated by filtering a suspension through a paper filter using a water-jet vacuum pump. The filtered powder was dried in a thin layer at 20°C in 48 h. The dried HAP powder, containing ammonium nitrate, was disaggregated in water in a planetary mill and then washed four times using distilled water and a paper filter.

The dried HAP powder was mixed with $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ in a ball mill with acetone; the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ was taken in a quantity that gave the prescribed ration HAP : NaH_2PO_4 (see Table 1). The acetone : powder : ball ratios were 1 : 1 : 5. After mixing the powder was dried at 20°C in 2 h and then passed through a sieve with 200 μm cells. Samples in the

TABLE 1.

Composition	Content, wt. %		Bulk density, g/cm ³	Mass losses, %, at 1150°C*
	HAP	NaH_2PO_4		
1	100	0	0.58	13
2	90	10	0.44	14
3	80	20	0.44	18
4	70	30	0.51	19

* According to data from thermal analysis.

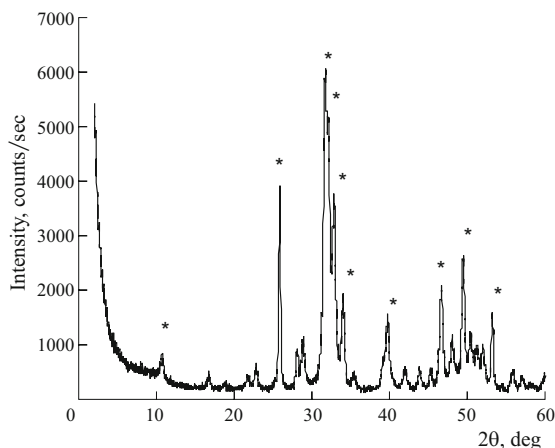


Fig. 1. XPA of HAP (*) powders after impurities have been washed out.

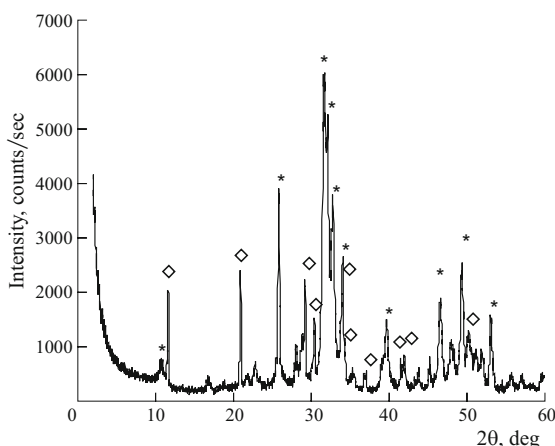


Fig. 2. XPA of powder 4, containing HAP and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, after milling: *) HAP; →) $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$.

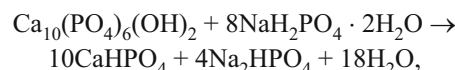
form of $6 \times (3 - 8)$ mm cylinders with mass $0.08 - 0.25$ g were pressed from the obtained powder in a hand press with a Teflon mold under specific pressing pressure 25 MPa. To investigate the changes of the phase composition of the power material the samples were sintered for 6 h at different temperatures in the interval $700 - 1200^\circ\text{C}$ with heating rate 5 K/min .

A Rigaku D/Max-2500 diffractometer (Japan) with a rotating anode was used to perform x-ray phase analysis on the samples. The data were obtained in reflection (Bragg – Brentano geometry) using $\text{CuK}_{\alpha\text{v}}$ radiation (average wavelength $\lambda = 1.54183 \text{ \AA}$). The data acquisition parameters were as follows: angle interval $2\theta = 10 - 110^\circ$, 2θ step 0.02° , recording rate $5^\circ/\text{min}$. The WinXPOW program with an ICDD PDF-2 database was used to perform qualitative analysis of the diffraction patterns obtained. A Perkin Elmer Pyris (Perkin Elmer, USA) thermal analyzer was used for thermogravimetric and DTA. The heating rate was 5 K/min and the temperature interval was $20 - 1150^\circ\text{C}$.

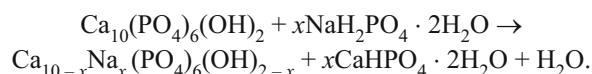
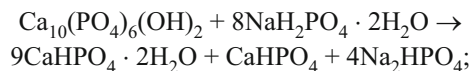
The XPA data show that HAP was obtained after synthesis and washing with water (Fig. 1). The size of the individual crystallites did not exceed 100 nm , which has a favorable effect on the sintering activity of the powders.

The bulk density of the mixtures was $0.44 - 0.58 \text{ g/cm}^3$ (see Table 1), and the density of the samples after pressing was $40 - 60\%$ of the HAP density (3.16 g/cm^3). The density of the samples after pressing increased with increasing content of sodium dihydrophosphate.

According to the XPA data, after the initial materials were mixed in a planetary mill HAP was found in the composition 1, 2, HAP together with a negligible amount of monetite in composition 3, and HAP together with brushite in composition 4. These data show that during milling HAP interacts with $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ for compositions 2 and 3 according to the reactions



and for composition 4 according to the reactions



Thus, according to the XPA data and the presumed reactions $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAP), $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , and Na_2HPO_4 are present in the mixes 2 and 3 while $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAP), $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , and Na_2HPO_4 are present in mix 4.

The XPA data for the mix 4 containing HAP and 30% $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ are presented in Fig. 2. HAP and brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ are easily determined in the diffraction pattern. Peaks due to monetite CaHPO_4 and Na_2HPO_4 , which are formed during the interaction, overlap with peaks due to the dominant compounds HAP and brushite.

The use of mechanochemical synthesis of calcium phosphates has been reported previously, but the reports dealt primarily with the synthesis of amorphous calcium phosphate with $\text{Ca} : \text{P} = 1.5$ or synthesis of magnesium- or carbonate-substituted HAP from CaO and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ or from $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{OH})_2/\text{Mg}(\text{OH})_2$ or from $\text{Ca}(\text{OH})_2/\text{MgCO}_3$ [7 – 9]. According to our data, the use of mechanochemical synthesis for obtaining calcium phosphates with $\text{Ca} : \text{P} = 1$ has never been previously reported.

According to thermal analysis data, as the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ content in the mixture increases, the total mass losses increase and range from 13% for HAP to 19% for the composition 4 (see Table 1).

The mass losses due to the removal of the adsorbed moisture and acetone to temperature 100°C are a common factor for all compositions. The mass losses at 200°C reflect

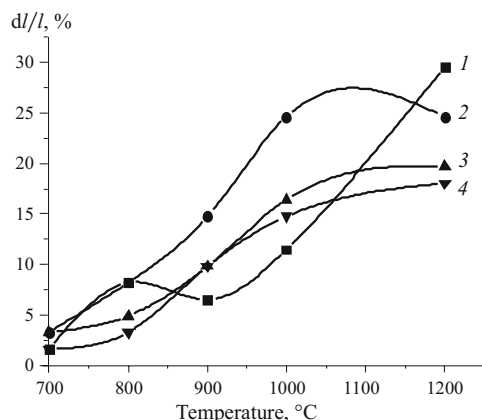
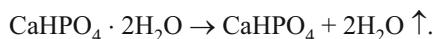
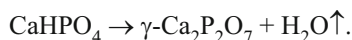


Fig. 3. Linear shrinkage of the samples after kilning for 6 h at different temperatures. The numbers on the curves correspond to the sample numbers.

the flow of the brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ decomposition reaction and the formation of monetite CaHPO_4 :



A transition of monetite into pyrophosphate occurs in the temperature interval 400 – 700°C:



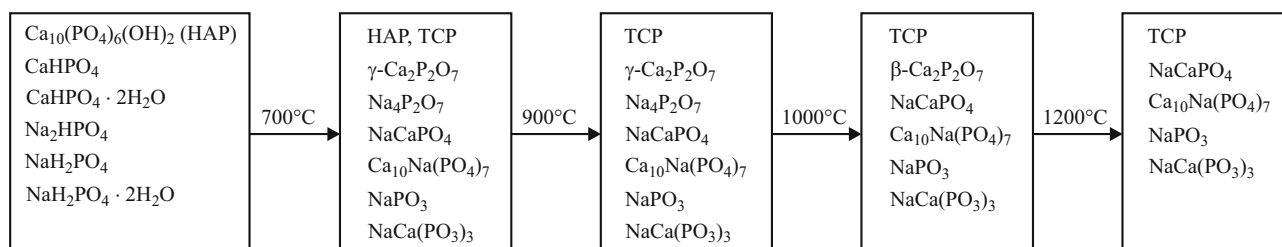
The small mass losses at temperature 700 – 800°C for the composition 1 reflect the transition of calcium-deficient HAP to TCP:



Since the synthesis was performed in air, CO_2 capture and its entry into the HAP structure in the form CO_3^{2-} are unavoidable. For this reason, a mass decrease could also be due to the decomposition of carbonate-HAP and removal of CO_2 , since it is well-known that CO_3^{2-} can occur even at temperatures below 850 – 900°C. After all carbonate groups have been removed, the subsequent mass losses could be due to partial dehydration of HAP with formation of oxyhydroxyapatite:



The phase composition of the samples based on HAP and NaH_2PO_4 before and after calcination is as follows:



According to XPA, TCP was observed in sample 1 after calcination at temperatures from 700 to 1200°C together with HAP. In the compositions containing HAP and NaH_2PO_4 , double sodium calcium phosphates can be expected to form on calcination. After calcination at 700°C a transition occurred from calcium hydrophosphate into γ -CPP and Na_2HPO_4 into sodium pyrophosphate:

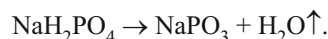


As the calcination temperature increases, a transition of HAP into TCP is observed in some cases. TCP can also form as a result of the interaction of HAP and CPP:



The interaction of calcium phosphates (HAP, TCP, CPP) with sodium phosphates results in the production of double sodium calcium phosphates — $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$ or NaCaPO_4 .

In addition, the NaH_2PO_4 remaining in the mixture loses water as temperature increases, transforming into sodium metaphosphate:



Next, sodium metaphosphate enters into reaction with calcium phosphates, forming $\text{NaCa}(\text{PO}_3)_3$.

The formation of the complex phase composition was accompanied by densification of the samples (Fig. 3). The greatest shrinkage (30%) was observed in samples based on the powder No. 1 (100% HAP). For samples based on a mixture of HAP and NaH_2PO_4 the shrinkage decreased with increasing NaH_2PO_4 content and constitutes 18 – 25% at 1200°C.

In summary, complex heterogeneous processes can occur in the HAP – NaH_2PO_4 powder system with intense mixing as well as with heat-treatment. The interaction of the main calcium orthophosphate ($\text{Ca} : \text{P} = 1.67$) and acidic sodium orthophosphate with mixing in acetone in a planetary mill results in the formation of monetite or brushite ($\text{Ca} : \text{P} = 1$). For high-temperature treatment, double sodium calcium ortho- and metaphosphates form in the experimental mixture.

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REFERENCES

1. T. V. Safronova, V. I. Putlyaev, M. A. Shekhirev, and A. V. Kuznetsov, "Composite ceramic containing a bioresorbable phase," *Steklo Keram.*, No. 3, 31 – 35 (2007); T. V. Safronova, V. I. Putlyaev, M. A. Shekhirev, and A. V. Kuznetsov, "Composite ceramic containing a bioresorbable phase," *Glass Ceram.*, **64**(3 – 4), 102 – 106 (2007).
2. M. N. Safina, T. V. Safronova, and E. S. Lukin, "Ceramic based on calcium phosphate with low sintering temperature, containing a resorbable phase," *Steklo Keram.*, No. 7, 19 – 24 (2007); M. N. Safina, T. V. Safronova, and E. S. Lukin, "Calcium phosphate based ceramic with a resorbable phase and low sintering temperature," *Glass Ceram.*, **64**(7 – 8), 238 – 243 (2007).
3. F. N. Lin, C. C. Lin, C. M. Lu, et al., "Mechanical properties histological evaluation of sintered Beta- $\text{Ca}_2\text{P}_2\text{O}_7$ with $\text{Na}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ addition," *Biomater.*, **16**, 793 – 802 (1995).
4. W. Suchanek, M. Yashima, M. Kakihana, and M. Yoshimura, " β -Rhenanite (β - NaCaPO_4) as weak interphase for hydroxyapatite ceramics," *J. Eur. Ceram. Soc.*, **18**, 1923 – 1929 (1989).
5. V. M. Vagabov, I. S. Kulaev, and T. V. Kulakovskaya, *High-Molecular Inorganic Polyphosphates: Biochemistry, Cellular Biology, Biotechnology* [in Russian], Nauchnyi Mir, Moscow (2005).
6. Yu. D. Tret'yakov (ed.), *Inorganic Chemistry, Vol. 2, Chemistry of Non-Transition Elements* [in Russian], Moscow (2004).
7. H. El. Briak-BenAbdeslam, M. P. Ginebra, M. Vert, and P. Boudeville, "Wet and dry mechanochemical synthesis of calcium phosphates influence of the water content on DCPD – CaO reaction kinetics," *Acta Biomater.*, **4**, 378 – 386 (2008).
8. C.-W. Chen, W. L. Suchanek, P. Shuk, et al., "The role of ammonium citrate washing on the characteristics of mechanochemical-hydrothermal derived magnesium-containing apatites," *J. Mater. Sci.: Mater. in Medicine*, **18**, 1413 – 1421 (2007).
9. W. L. Suchanek, K. Byrappa, P. Shuk, R. E. Riman, et al., "Mechanochemical-hydrothermal synthesis of calcium phosphate powders with coupled magnesium and carbonate substitution," *Solid State Chem.*, **177**, 793 – 799 (2004).